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NMR Identification of Substitutional Isomers in
Chelated Polycyclic Aromatic Systems

by

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NMR IDENTIFICATION OF SUBSTITUTIONAL ISOMERS IN
CHELATED POLYCYCLIC AROMATIC SYSTEMS¹

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Some time ago we made a study of chemical shifts in chelated phenols which contain the structure I, where Y = -H, -CH₃ and -OCH₃, and from the results obtained,³ it seems likely that magnetic resonance methods may be

(3) A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, J. Am. Chem. Soc., 82, 5057 (1960).

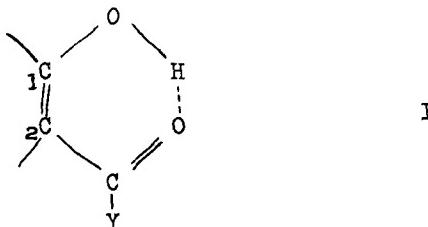
useful in distinguishing between isomers of phenols with chelating substituents. The arguments which we will employ can easily be extended to other systems. The results exhibit two aspects by means of which the isomers may be distinguished on the basis of their high-resolution proton magnetic resonance spectra: (a) From the -OH proton chemical shift. In aromatic systems, the shift of a chelated -OH proton relative to the -OH peak in the corresponding parent phenol is quite large. We have found that this chemical shift is a linear function of the bond order of bond ₁C = ₂C, with the slope depending somewhat upon the substituent Y.³ If the shift is measured, then that part of the aromatic nucleus spanned by the chelated structure can be identified.

(b) From the chemical shift of the protons in Y. A large part of the chemical shift of a proton, which is situated near an aromatic system, arises from the π -electronic ring currents induced in the aromatic system when the molecule is placed in a magnetic field.^{4,5} It is this effect which leads to the other

(4) J. A. Pople, J. Chem. Phys., 24, 1111 (1956).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance (McGraw-Hill Book Company, Inc., New York, 1959).

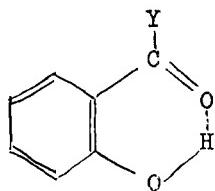
method of assigning the substituent position in polynuclear aromatic systems.



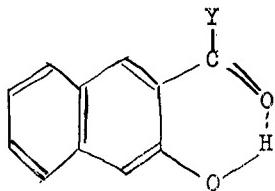
Method (a) is straightforward, direct, and requires little amplification.³ Method (b) we will discuss in more detail. To a first approximation, the π -electron currents induced in each six-membered ring can be replaced by an elementary dipole situated at the center of the ring. Each dipole exerts a secondary magnetic field at Y, which is inversely proportional to the third power of the distance between the dipole and Y. This secondary field is in the same direction as the applied magnetic field, provided Y lies in the same plane as the aromatic system. If Y does not lie in this plane, then the effective field is reduced until, eventually, the applied field may be opposed by a secondary field. The maximum opposition to the applied field occurs when Y lies on the perpendicular drawn through the center of the dipole.

It is quite easy to show^{4,5} that when Y does lie in the same plane as the aromatic system, then each secondary field causes a chemical shift of about $27.58/r^3$ parts per million if r, the distance from the protons or other magnetic nuclei in Y to the π -electronic dipole, is expressed in Angstrom units. Hence, if the dimensions of the molecule are known, the approximate relative chemical shifts of Y may be predicted for a series of similar compounds. These predicted shifts will be only approximately correct, because the π -electron systems are perturbed to different extents by interaction with the substituents, and this interaction, in its turn, modifies the diamagnetic circulations induced in the substituents. However, these effects are less important than the geometrical considerations outlined above, and they do not affect the qualitative arguments that are used.

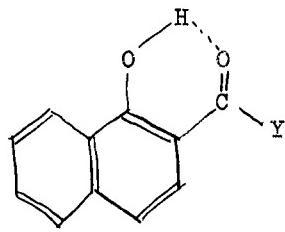
The ring current shifts will be modified by solvent interactions, and so our arguments apply to solutions in which the solvent interactions are either negligible or very similar for the solutes in question.



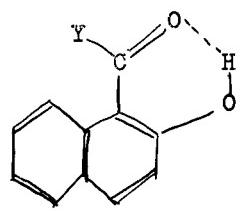
II



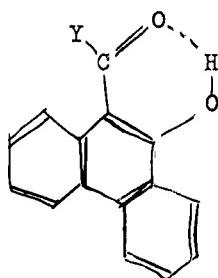
III



IV



V



VI

With this qualification, one predicts that the downfield, ring-current shifts in compounds of types II to VI of the $\text{Y} = \text{H}$ proton absorption peaks should be about 0.175 p.p.m. on going from II to III, somewhat less on going from II to IV, and about 0.55 p.p.m. on going from II and III to V and VI. These predictions are in reasonable agreement with the observed shifts which in τ' units are

	II	III	V	VI
$\text{Y} = \text{H}$	0.04	-0.09	-0.71	-0.57

Here, negative values are downfield with respect to positive. These, and the other measurements given below, were made on dilute solutions in carbon tetrachloride using cyclohexane as an internal reference.³ The shifts were converted to the tetramethylsilane τ' scale by using a τ' value of 8.51 for cyclohexane.

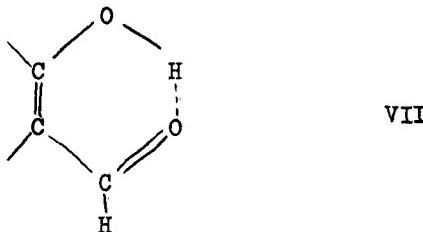
In the case of the corresponding ketones, $\text{Y} = \text{CH}_3$, prediction of the ring current shifts is complicated by rotation about the $\text{C}-\text{CH}_3$ bond, but similar principles hold. The relative chemical shifts, however, will be smaller within this series than in the case of the aldehydes because the protons of the $-\text{CH}_3$ group are further away from the elementary induced dipoles and they do not lie in the same plane as the aromatic system. The observed shifts of the $-\text{CH}_3$ absorption peaks in τ' units are

	II	III	IV	V	VI
$\text{Y} = \text{CH}_3$	7.35	7.21	7.23	7.14	7.19

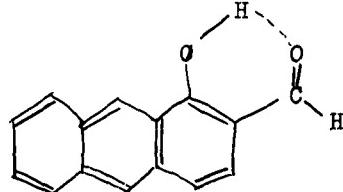
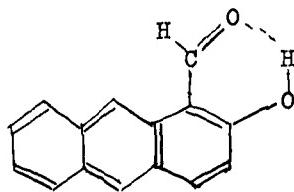
in qualitative agreement with the above arguments.

As an example of the use of these methods in structural determination, consider the position to be assigned to the $-\text{CYO}$ groups in an hydroxyanthral-dehyde (A) and in an hydroxy-anthranyl-methyl ketone (B) which melt at 167°C

and 116°C respectively. The $-\text{OH}$ proton line of A occurs at $\tau = -3.64$. This position is about 8.7₅ p.p.m. down-field from that expected³ for the $-\text{OH}$ position in either 1-hydroxy, or 2-hydroxyanthracene ($\tau \approx 5.1$) and is at the position expected for the chelated system VII.



in which the mobile bond order of the $\text{C}=\text{C}$ bond is 0.745.³ Hence, it follows that the $-\text{OH}$ and aldehyde group are chelated and that the chelated system must span the 1-2 bond in the anthracene nucleus. It can not span the 2-3 position, i.e. A is either VIII or IX.

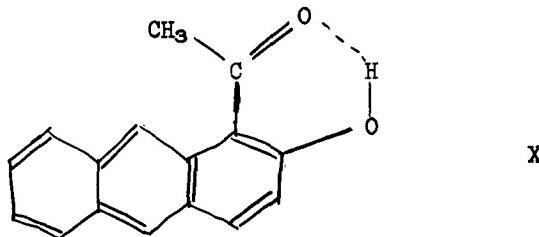


The ring current effects enable us to distinguish between these two structures. The observed position of the $-\text{CHO}$ absorption peak, $\tau = -0.87$, is in the range predicted for structure VIII. For structure IX, the $-\text{CHO}$ τ value is predicted to be about -0.1, which differs so greatly from experiment that VIII must be the correct structure. This conclusion supports a structural determination based upon chemical arguments.^{6,7}

(6) J. L. Ferrari and I. M. Hunsberger, *J. Org. Chem.*, 25, 485 (1960).

(7) J. L. Ferrari, Ph.D. Thesis, Fordham University, 1962.

In a similar way, the -OH and -CH₃ chemical shifts, τ = -4.37 and 7.18 p.p.m. respectively, show³ that B is X.



Experimental

The samples and experimental procedure, with one exception, were the same in these experiments as described in an earlier report.³ The exception is the hydroxyanthraldehyde (A), the synthesis of which has been described elsewhere.^{6,7} Furthermore, we are indebted to Professor I. Moyer Hunsberger for furnishing the samples.

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